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Novel Multi-Stage Three-Dimensional Deployment Employing Ionoprinting of Hydrogel Actuators

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ABSTRACT

Novel multi-stage adaptive morphing of a hydrogel cube has been achieved by combining multi-metal ionoprinting and redox chemistry of iron. A demonstration of the two-stage deployment has been shown for (1) the selective opening and closing of the cube's lid, where the hinge point has been ionoprinted with iron, and (2) the full unfolding and folding of the cube into its cruciform net, with remaining hinges ionoprinted with vanadium. The selective unfolding and folding is achieved by alternating the oxidation state of iron between +2 and +3. This is achieved using redox chemistry selective for iron. This approach could be applied, in principle, to more degrees of staging by adding additional redox responsive ionoprinted cations and appropriate selection of reducing agents.

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks that can be highly swollen in water to form a gel that has a water content approaching 99%; they are also able to respond to a range of stimuli including pH, temperature, light and ionic strength [1]. Their use as actuation materials and structures for biomedical and soft-robotics applications has been widely studied recently; with the desired actuation pathway often being created by inhomogeneity to the material or structure either during construction or synthesis, or as presented here, programmed into the material post construction or synthesis [2–5].

Ionoprinting is a technique used to pattern metal cations into the surface and near surface of a hydrogel using an electric potential. The localized deposition of metal cations creates regional ionic crosslinking resulting in volumetric changes in the hydrogel, giving rise to a controlled variation in mechanical performance of the system. This patterning technique introduces localized stress within the hydrogel which can be used to create folding patterns for the actuation and morphing of different geometries [6].

The easily accessible oxidation states of iron have been used by different research groups to induce variable strength ionic crosslinking for shape-memory, self-healing, and sol-gel transition [5,7–10]. Iron(III) cations can be described as “hard” cations binding strongly to oxygen atoms in negatively charged ligands over others; while iron(II) cations are “soft” cations which prefer to bind to neutrally charged ligands [11]. The two oxidation states of iron are separated by reduction potential of 0.771V [12].

Hierarchical multi-step folding of hydrogel bilayers has been achieved by G. Stoychev *et al.* by use of an active hydrogel layer and passive polymer layer [13]. The hierarchical multi-step folding behavior is created and controlled by the diffusion front and the shape of the bilayer, resulting in a system in which the actuation pathways are predetermined and un-programmable, which ultimately limits its allowed transitions and applications.

Conversely, Y. Mao *et al.* have successfully created sequential self-folding structures using shape memory polymers (SMPs) with variable glass transition temperatures (T_g) [14]. By blending TangoBlack™ and VeroWhite™ resins, in different ratios in a multi-material 3D printer, SMPs with variable T_g can be produced and printed into a single structure. In this study, the SMPs were printed as the hinges of the structures and then fixed into their temporary shape by heating the SMPs above all their T_g , before deforming, then cooling below their T_g for fixation. The original shape is restored by submerging the structure into a water bath held above the SMPs T_g with the hinges folding in order of increasing T_g .

Similarly to Mao *et al.* we are interested in developing a 4D material which employs a chemical stimuli (i.e. the triggered sequential reduction of metal cations) to create the same active folding effect achieved with SMPs. In our work, we utilize hydrogels, containing high metal binding affinity phosphate functional groups, which are able to undergo multi-stage deployment through the use of multi-metal ionoprinting and selective redox chemistry of iron. By ionoprinting with a variety of different metals, ionic crosslinking with different susceptibility to either reduction or oxidation can be created, by combining ionoprinting of iron and vanadium this has been achieved. Iron(III) can be selectively reduced to iron(II) with ascorbic acid, where iron(III) is created by ionoprinting by oxidation of iron(0). The selective redox reactions allow for selective unfolding and re-folding of the iron ionoprinted hinges, while all hinges can be unfolded and re-folded through submerging into a relative non-polar and polar solvent, respectively.

EXPERIMENTAL

Materials: Phosphoric acid 2-hydroxyethyl methacrylate ester (PHMA), 2-Hydroxyethyl acrylate (HEA), N,N'-Methylenebisacrylamide (MBAA), 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and triethylamine (TEA) were obtained from Sigma-Aldrich (Poole, UK). L(+) ascorbic acid (AA) was purchased from Alfa Aesar (Heysham, UK). 2-(methacryloyloxy)ethyl phosphate (MOEP) was extracted from PHMA with n-hexane and HEA was filtered through basic alumina, while all other chemicals were used without further purification.

Preparation of hydrogels: The monomers (HEA and MOEP) were combined in a molar ratio of 4:1, respectively, before being neutralized with TEA. Crosslinker (MBAA) and photoinitiator (DMPA) were added prior to dissolution with water:DMSO (2:1, v/v), resulting in a precursor solution with total monomer, crosslinker and photoinitiator of concentration of 2.5M, 12.5mM and 3.0mM, respectively. The precursor solution was degassed and then poured into molds (1mm thick) and sealed with glass slides prior to curing under a UV lamp (365/245nm, 4W) for 2 hours. Hydrogels were soaked in frequently changed di-ionized water prior to further testing.

Ionoprinting: Hydrogels swollen in 0.1 M LiCl solution for a minimum of 48 hours, were patted dry prior to ionoprinting. Superficially dry samples were ionoprinted between an aluminium foil cathode and a vanadium or iron anode using a DC Power Supply.

Conditions to induce actuation: The solutions used to achieve actuation of the hydrogels were: 0.2M ascorbic acid; EtOH:Ac 1:1 v/v & DI water. With actuation times of 20 mins for all except EtOH:Ac, which took 2 hours.

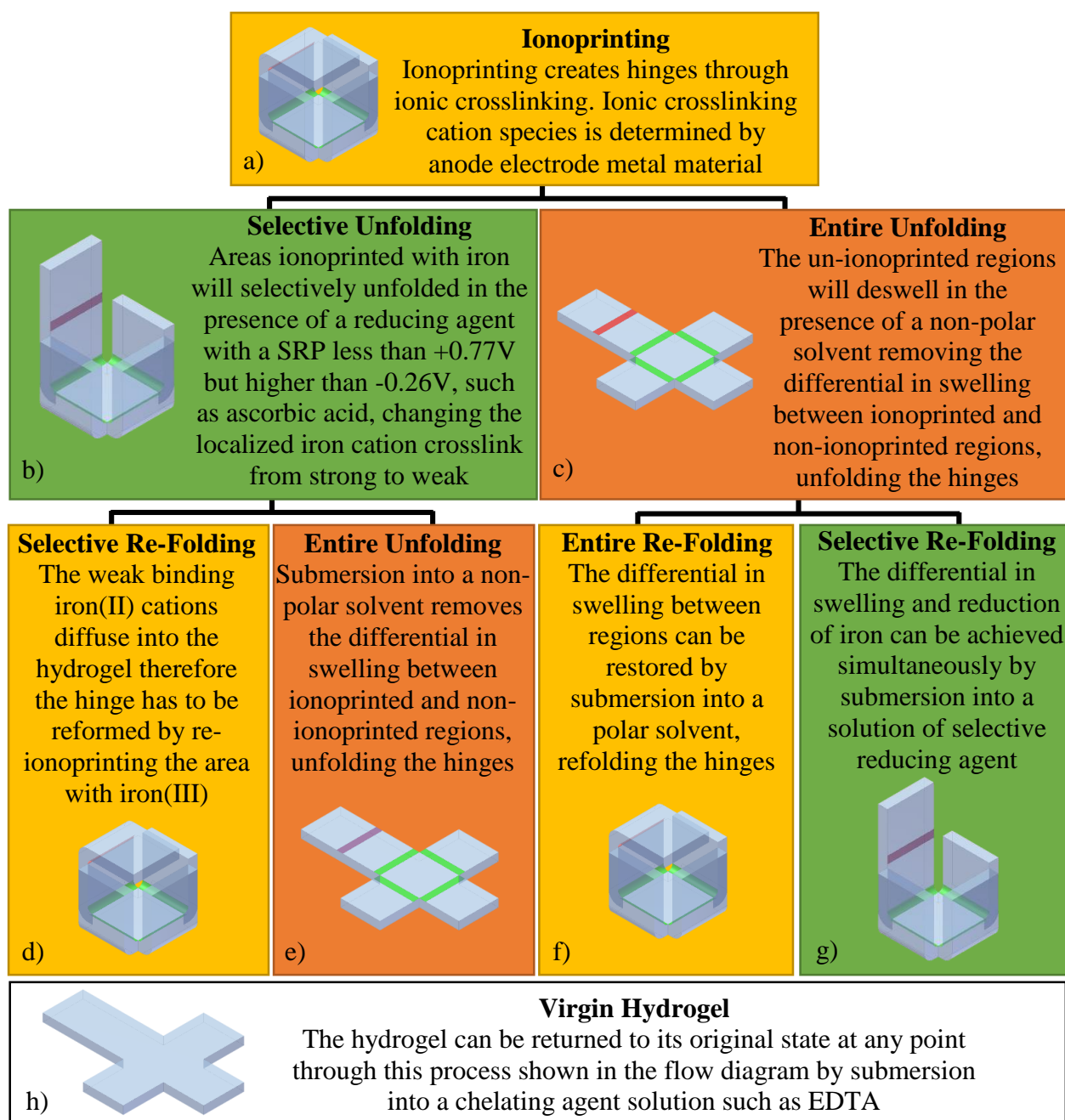


Figure 1: Schematic flow diagram of two-staged deployment of an ionprinted cube. Ionprinted with vanadium and iron from a flat cruciform.

RESULTS & DISCUSSION

Until now, ionoprinting has only been performed with one metal at a time, here we present ionoprinting of two different metals into the same hydrogel. Through the controlled ionoprinting of the two metal cations, the 4D response of the hydrogel can be programmed by considering their relative ionic crosslinking strengths, their susceptibility to redox, and the availability of the different oxidation states.

The example illustrated in Figure 1 and 2 uses ionoprinting of vanadium and iron to create a

cube that can undergo selective and entire unfolding depending on the stimuli. Each of these configurations can be switched to the other or be returned to a cube, by the appropriate selection of stimuli, as shown and explained in Figure 1 and 2.

The opening of the lid of the cube is achieved by selective reduction of the iron ionoprinting hinge, the only hinge that is not at the base, as shown in Figure 1 and 2 (a) to (b). The selective reduction is achieved using ascorbic acid as an oxidizing agent. The standard reduction potential (SRP) between dehydroascorbic acid and ascorbic acid is +0.06V and therefore ascorbic acid will reduce and itself be oxidized by anything with a SRP greater than this [15]. The SRP between iron(II) and iron(III) is +0.771V, while between vanadium(III) and vanadium(II) it is -0.255V, therefore the only ionoprinted hinge present that can be reduced is iron. The difference in the swelling ability and ionic crosslinking strength between iron(III) and iron(II) has been studied previously, with the difference in swelling shown to be 48% and 69% respectively, of the potential swelling of lithium chloride solution [16]. Through this relative difference in swelling ability, and the “soft” nature of iron(II) cations, the cations diffuse into the hydrogel and surrounding solution, resulting in the complete unfolding of the iron hinge.

In the present system, the ability of the lid to move to a new configuration simply by re-oxidizing the iron(II) cations back to iron(III) is not viable since the “soft” cations have a tendency to diffuse away from the localized hinge region into the surrounding bulk hydrogel. Therefore to recreate the localized iron(III) ionic crosslinking the hinge must be re-ionoprinted, as shown in Figure 2 and 1 (b) to (d).

The bulk of the hydrogel is hydrophilic and therefore will swell in polar solvents e.g. water and deswell in less polar solvents e.g. ethanol and acetone. The deswelling of the bulk hydrogel will remove the swelling differential created through ionoprinting, unfolding the entire cube as shown in Figure 1 and 2 (b) to (e) and (a) to (c). The entire cube can be re-folded by restoring the differential between the ionoprinted and non-ionoprinted regions by re-swelling the bulk of the hydrogel with a polar solvent, as shown in Figure 1 and 2 (c) to (f.)

By combining the selective reductive power of ascorbic acid and the hydrogel swelling induced by water, the previous deswollen cube can be reactivated such that the lid can be opened by using a solution of ascorbic acid, as shown in Figure 1 and 2 (c) to (g).

Based upon the results to date, the authors believe this approach could be applied to a variety of other metallic systems to create higher levels of staged deployment. For example, ionoprinting iron(III), vanadium(III) and aluminum(III) would allow for three staged deployment. With the first, second and third stages being achieved by using a reducing agent with SRP between +0.771V to -0.255V and +0.771V to -1.676V and non-polar solvent, respectively. The work presented has demonstrated the creation of a 4D material, which employs a chemical stimulus (i.e. the triggered sequential reduction of metal cations) to create active folding of geometric forms using two-staged deployment of a hydrogel.

CONCLUSIONS

Through the combination of ionoprinting of multiple metals and redox chemistry, staged hydrogel actuation has been achieved. This work has demonstrated the selective and full folding and un-folding of cube using ionoprinting with iron and vanadium. The iron when ionoprinted is oxidized to oxidation state +3, which is a “hard” cation but can be reduced to oxidation state +2 a “soft” cation – this transition results in a relative increase in swelling, and a decreased ionic crosslinking strength yielding reduced localized stiffness permitting the unfolding of the ionoprinted hinge. The hinge can be successfully refolded by oxidizing iron to oxidation state +3

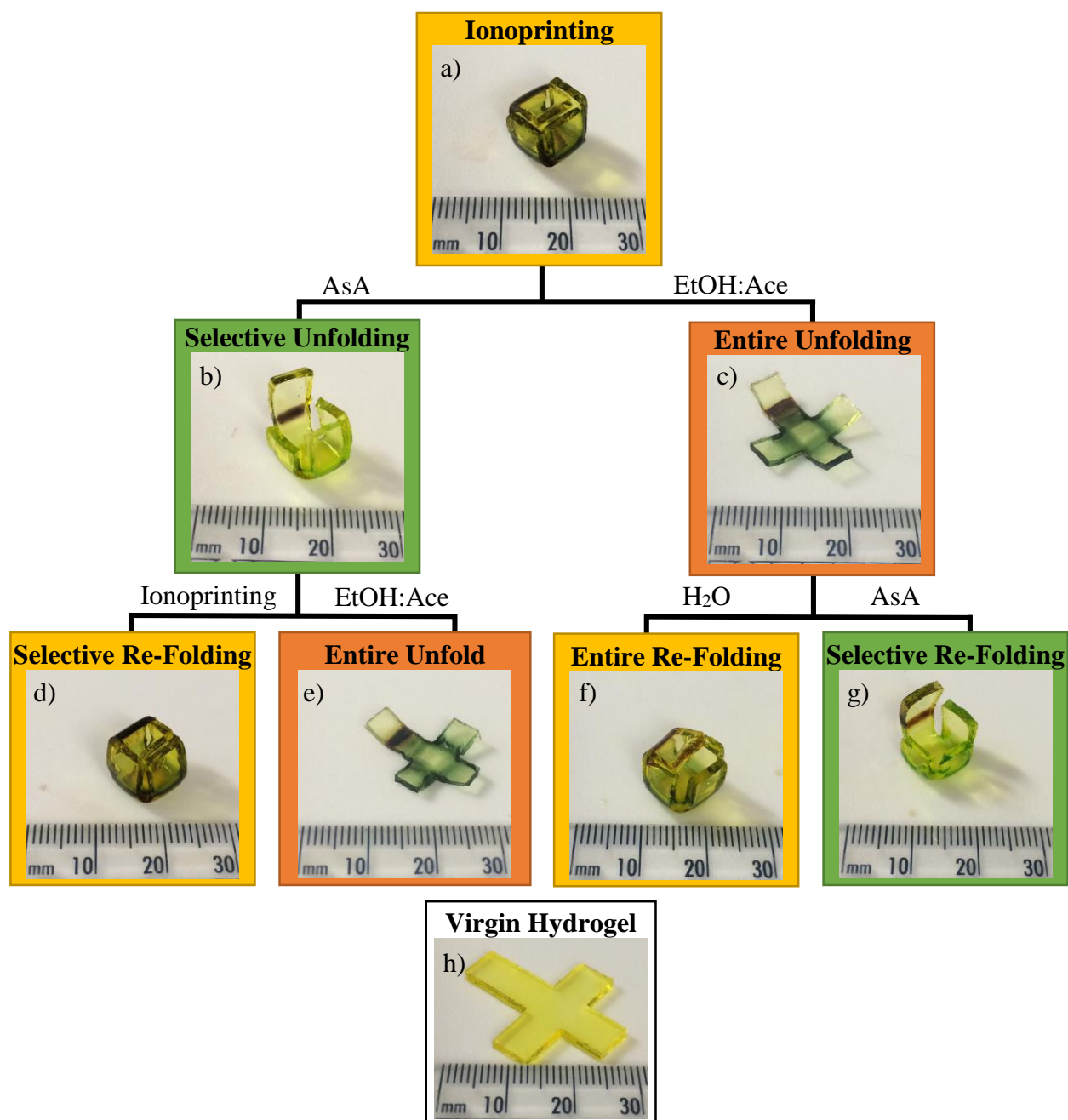


Figure 2: Flow diagram of experimental two-stage deployment shown in Figure 1

by ionoprinting for a second time. This methodology permits the selective and reversible actuation of a model 4D material. In principle, this approach could be extended further to create higher staged deployment through different combinations of metal cations exhibiting “hard” and “soft” oxidation states.

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